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I, JONNE YABSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PR 4651 for a patent by VARIAN AUSTRALIA PTY LTD filed on 27 April 2001.

WITNESS my hand this
Twenty-first day of March 2002

A handwritten signature in cursive script that reads "J R Yabsley".

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AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

APPLICANT: VARIAN AUSTRALIA PTY LTD

Invention Title: “*MASS SPECTROMETER*”

The invention is described in the following statement:

IP Australia
Documents received on

27 APR 2001

Batch No:

Melbourne

MASS SPECTROMETER

Technical Field

5 The present invention relates to a mass spectrometer that includes a quadrupole mass analyser. The invention will be described mainly with reference to an inductively coupled plasma-mass spectrometer (ICP-MS) having an inductively coupled plasma ion source, however it is to be understood that the invention encompasses other types of mass spectrometers employing other types of ion sources.

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Background

Published International Application WO 00/17909 (PCT/AU99/00766), the disclosure of which is to be taken as incorporated herein by this cross-reference, discloses a mass spectrometer having an ion reflecting instead of an ion transmissive optics system. The spectrometer includes an ion source for providing a beam of sample particles and an ion optics system between the source and a mass analyser for establishing a reflecting electrostatic field for reflecting ions from the beam through an angle, for example 90°, and for focussing them into the mass analyser entrance.

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It has been found that the invention of WO 00/17909 as embodied in an ICP-MS instrument gives excellent sensitivity for detection of elemental isotopes having relatively high atomic masses (for example, the sensitivity for thorium, atomic mass 232, was over 650,000 counts per second per microgram per litre). However the sensitivity for elemental isotopes having low atomic masses is relatively poor (for example the sensitivity for beryllium, atomic mass 9, was less than 10,000 counts per second per microgram per litre). Furthermore, the background count rate (the count rate detected at a selected mass-to-charge ratio when no ions having that selected mass-to-charge ratio were expected to be present) was higher than desired, and when the voltages applied to the ion optics electrodes were increased to improve the focussing to increase sensitivity for detection of low atomic mass isotopes, the background count rate unfavourably increased.

30

The best possible Limit of Detection (LOD) for an elemental isotope in an ICP-MS is given by

$$\text{LOD} = 3 \times (\text{background count rate/measurement time})^{1/2} / \text{sensitivity}$$

5 Thus the relatively high background count rates and relatively low sensitivities for elemental isotopes having low atomic masses means that detection limits for such low atomic mass isotopes are undesirably high.

10 Although this problem has been highlighted by use of a mass spectrometer which employs a reflecting ion optics system, it is considered (in view of what is thought to be the mechanism for causing the high background count rates, as explained hereinbelow) that the same problem would exist in mass spectrometers that do not use a reflecting ion optics system.

15 The discussion herein of the background to the invention is included to explain the context of the invention. This is not to be taken as an admission that any of the material referred to was published, known or part of the common general knowledge in Australia as at the priority date established by the present application.

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 An object of the present invention is to provide a mass spectrometer that employs a quadrupole mass analyser which has an improved (that is, a low) limit of detection for elemental isotopes of low atomic masses. The mass spectrometer may employ either a transmissive or reflecting ion optics system.

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Summary of the Invention

 According to the invention there is provided a mass spectrometer for elemental analysis of a sample including a source for providing a beam of particles including ions representative of chemical elements in the sample, a
30 quadrupole mass analyser and an ion detector for receiving ions from the beam of particles for spectrometric analysis whereby concentrations of different elements in the sample are determinable, an ion optics system for establishing an electrostatic field between the source and the quadrupole mass analyser, and a quadrupole ion guide located adjacent the entrance to the quadrupole

mass analyser, wherein the electrostatic field directs the ions along a path into the ion guide thereby separating said ions from neutral particles in the beam of particles, the quadrupole ion guide having electrodes which are configured to divert said ions from said path prior to their passage through the quadrupole mass analyser and which shield the mass analyser entrance as viewed in the direction of said path.

According to a preferred embodiment of the invention there is provided a mass spectrometer for elemental analysis of a sample including a source for providing a beam of particles including ions representative of chemical elements in the sample, a quadrupole mass analyser and an ion detector for receiving ions from the beam of particles for spectrometric analysis whereby concentrations of different elements in the sample are determinable, an ion optics system for establishing a reflecting electrostatic field between the source and the quadrupole mass analyser for reflecting ions from the particle beam thereby separating said reflected ions from neutral particles in the beam of particles, and a quadrupole ion guide located adjacent the entrance to the quadrupole mass analyser, wherein the reflecting electrostatic field directs the reflected ions along a path into the ion guide, the quadrupole ion guide having electrodes which are configured to divert said reflected ions from said path prior to their passage through the quadrupole mass analyser and which shield the mass analyser entrance as viewed in the direction of said path.

It has been surprisingly discovered that the use of the ion guide immediately in front of the mass analyser significantly improves the limit of detection for elemental isotopes of low atomic masses. This is principally because the ion guide has the effect of reducing the background count rate to a very low figure, even when the voltages of the preceding ion optics elements are set to values that favour the transmission of isotopes of low atomic masses. Without the ion guide the background count rate at such voltages is unacceptably high. Use of the ion guide thus permits an increase in sensitivity for low mass isotopes along with a decrease in the background count rate. Both these factors contribute to the improved limits of detection for isotopes of low atomic mass. It is thought that the reduction of the background count rate is

due to the ion guide preventing the entry of energetic neutral particles into the quadrupole mass analyser, such energetic neutral particles possibly being produced by acceleration of the sample ions through residual gas in the spectrometer, which can occur whether those sample ions are directed by either
5 a transmissive or reflecting ion optics system. That is, it is thought that acceleration of the ions through the residual gas in the vacuum system causes some of those ions to interact (for example by resonant charge exchange) with atoms of the residual gas and so produce high energy neutral atoms which, were they to enter the mass analyser, would interact with metal surfaces they
10 might strike and so generate ions that pass into the detector, thus increasing the background count rate. The configuration of the ion guide therefore is such that it causes a diversion of the sample ions that is sufficient to prevent entry of so produced high energy neutral atoms into the mass analyser. That is, the configuration is such that any ions that may happen to be neutralised will
15 continue in a ballistic trajectory that results in them striking an electrode element of the ion guide and so prevent them from reaching the ion detector.

In the following description the ion guide electrodes are sometimes termed "fringe rods", although they may not necessarily be rods as such. This is
20 because it is known to place a set of ion guiding rods at the entrance of a quadrupole mass analyser to transmit the ions efficiently into the mass analyser. In the absence of such an ion guide the entry of ions into the mass analysing quadrupole would be inhibited by the 'fringing fields' that exist at the entrance of a quadrupole mass analyser. The known ion guide rods provided to
25 assist the entry of ions into the quadrupole mass analyser are often called fringe rods. The ion guide electrodes of this invention serve that function as well as shielding the ion detector from high-energy neutral particles that might otherwise accompany the ions into the mass analyser

30 It is considered there could be two components to the motion of any energetic neutral particle that might have been formed by resonant charge exchange between a high-velocity ion and the background gas. The more obvious component would lie along the direction of travel of the ion beam as it entered the ion guide electrodes. The other, less obvious, component would lie

along the direction of travel that the ion was following at the instant that the charge exchange occurred. Ions travelling through a space surrounded by the ion guide electrodes or fringe rods are subject to sinusoidal acceleration by a radiofrequency electromagnetic field applied to the electrodes. This sinusoidal acceleration has a component in a direction perpendicular to the path lying along the geometric centre of the electrode assembly, as defined by the point of intersection of the two lines connecting the centre of one electrode of each pair to that of the diametrically opposite electrode. The orientation and configuration of the quadrupole ion guide with respect to the trajectory of the incoming ion beam is chosen to shield the ion detector from neutral particles having either of the two possible components of motion just described.

Preferably the quadrupole ion guide comprises four elongate electrodes which are curved to thereby define a curved diversionary path for the ions. Alternatively non-curved fringe rods may be provided, an example of such an arrangement being described herein below.

Preferably, with curved elongate electrodes, the electrodes are configured such that the ions exit the quadrupole ion guide generally in the same direction as said path along which they enter the quadrupole ion guide.

Thus it is advantageous to configure the curved ion guide electrodes in such a way that the entrance end and the exit end of the ion guide are parallel but not co-linear, being joined by a gently curved section that is approximately the shape of a distorted letter 's'. Other configurations are possible so long as the ions are focussed through an aperture and enter the ion guide electrodes in front of the mass analyser, said electrodes being so configured that they act to guide the ions along a path that is different from that followed by neutral particles entering the arrangement. Such neutral particles are thereby prevented from entering the mass analyser and subsequently producing ions that would be detected and contribute to the background count rate.

Preferably the ion guide is configured such that, viewed in the direction of entry of ions into the ion guide, the electrodes completely cover the detector

entrance. That is, the orientation of the curved quadrupole ion guide is such that if at any place the direction of curvature of an electrode is such that an ion accelerated by the RF fields applied by the electrodes might be accelerated in the direction of the ion detector, an electrode lies between the accelerated ion and the detector. This ensures that the ion detector lies in the shadow of an electrode in the event that an accelerated ion becomes a neutral particle by resonant charge exchange with the background gas. This provides very efficient shielding of the ion detector from neutral particles.

For a better understanding of the invention and to show how it may be carried into effect, embodiments thereof will now be described, by way of non-limiting example only, with reference to the accompanying drawings.

Brief Description of Drawings.

Fig. 1 schematically illustrates a mass spectrometer according to a preferred embodiment of the invention.

Figs. 2 to 5 schematically illustrate respective alternative embodiments of the invention having different ion guide configurations.

Figs. 6A and 6B are schematic plan and end views respectively of the rods of an ion guide of the Fig.1 embodiment.

Detailed Description

Fig. 1 shows a mass spectrometer 10 that includes ion production means 12 which is preferably an atmospheric plasma ion source such as an inductively coupled plasma torch. Ion production means 12 is supplied by known means (not shown) with a representative portion of an analytical sample (not shown) and produces a plasma 14 that contains ions representative of the chemical elements present in the analytical sample. The plasma 14 impinges on an aperture 16 in a cooled sampler cone 18. Aperture 16 preferably has a diameter of 1 millimetre and provides an entry into a chamber 20 that is connected through a port 22 to a first vacuum pump (not shown). The pressure in chamber 20 is preferably in the range 2 Torr to 4 Torr. A representative

portion of plasma 14 passes through aperture 16 and forms a free jet expansion (not shown). An aperture 24 in a skimmer cone 26 preferably has a diameter of 0.5 mm and is co-axial with aperture 16. The distance between apertures 16 and 24 is preferably in the range 6 to 9 mm. Aperture 24 provides an entry from chamber 20 into a second chamber 28 (shown in part) that is connected through a port (indicated by arrow 30) to a second vacuum pump (not shown). The pressure in the second chamber 28 is preferably in the range 0.0001 Torr to 0.0003 Torr. A representative portion of the free jet expansion passes through aperture 24 into the second chamber 28.

A first electrode 32 is located downstream of aperture 24. Electrode 32 is preferably cylindrical and has its axis on an extension of a line joining the centres of apertures 16 and 24. Electrode 32 is preferably at a potential adjustable in the range -300 to -400 volts. A second electrode 34 preferably in the form of a plate with a central aperture is located downstream of the first electrode 32. The centre of the central aperture in electrode 34 lies on the extension of the line joining the centres of apertures 16 and 24, so that electrodes 32 and 34 are co-axial. Electrode 34 is preferably at the same potential as electrode 32. A third electrode 36 preferably in the form of a hollow cylinder mounted on a plate having a central aperture of the same diameter as the internal diameter of the hollow cylinder is located downstream of electrode 34 and is co-axial therewith. Electrode 36 is positioned as indicated in Fig. 1 with the plate downstream of the hollow cylinder. Electrode 36 is preferably at a potential adjustable in the range -100 to -1000 volts.

The combined effect of electrodes 32, 34 and 36 is to produce a beam of positive ions 38. As ion beam 38 travels along the extension of the line passing through the centres of aperture 16 and 24 and the centres of electrode 32, 34 and 36, it is accompanied by a beam of energetic neutral particles and of light from plasma 14. Ion beam 38 is made to follow a different path from said neutral particles and the light by the combined effects of electrode 36, an electrode 40 and an ion mirror 42. Ion mirror 42 is preferably in the form of a flat ring having four isolated electrode segments thereon (not shown), one electrode segment being located in each of the four quadrants of said ring.

Each of the four electrode segments is preferably provided with an independently adjustable potential in the range of 0 to +400 volts. Ion mirror 42 is located so that the line joining the centre of one electrode segment to the centre of the diametrically opposite segment is perpendicular to the extension of the line passing through the centres of apertures 16 and 24 and the centres of electrodes 32, 34 and 36. Electrode 40 is preferably a flat plate and is supplied with an adjustable negative potential, preferably in the range -140 to -1400 volts. By appropriate adjustment of the potentials applied to electrodes 32, 34, 36 and 40 and to each of the four independent electrode segments of ion mirror 42, ion beam 38 can be directed (reflected) into an aperture 44. Any photons or energetic neutrals that originally accompanied ion beam 38 as it emerged from electrode 36 continue in their original direction and proceed through the large central aperture of ion mirror 42. These photons and energetic neutrals are therefore not able to reach an ion detector 46 and thus cannot cause any output from detector 46. Any output from detector 46 that arises from anything other than ions of an elemental isotope of interest is undesirable because it degrades the detection limit for said elemental isotope.

Aperture 44 leads into a third vacuum chamber 48 connected through a port 50 to a third vacuum pump (not shown) that keeps the third chamber 48 at a pressure preferably less than 0.00001 Torr. Chamber 48 contains a quadrupole mass analyser 52 consisting of two pairs of rods (one pair is shown as 54) and a quadrupole ion guide 56, consisting of corresponding pairs of electrodes (one pair is shown as 58) in front of the mass analyser 52 at its entrance 55. An exit aperture 60 and the ion detector 46 are placed in the third chamber 48 to receive ion beam 38 for mass spectrometric analysis, as is known in the art.

Electrodes 58 of ion guide 56 are shaped and positioned so that there can be no direct path from aperture 44 to ion detector 46. For example, Fig. 6 shows a preferred arrangement of the four fringe rods of the ion guide 56 of the embodiment of Fig. 1. Fig. 6A shows a plan view while Fig. 6B shows a view from a direction of the arrow V in Fig. 6A (the entrance ends of the fringe rod electrodes being shown shaded). Ion beam 38 enters the space between

electrode pairs 58 and 58A along the direction of arrow V. Each pair of opposite fringe electrodes 58 and 58A is supplied with the same radio frequency voltage as its corresponding pair of mass analyser rods 54, preferably by means of a suitable capacitor (not shown) connecting each pair of mass analyser rods 54 to its corresponding pair of electrodes 58. Under the influence of this radio-frequency voltage, ions in ion beam 38 pass through the space surrounded by fringe electrodes 58 and 58A and enter the space surrounded by mass analyser rods 54. As is known in the art, the path of ions through this space is determined by the radio frequency (RF) and DC voltages applied to the rods 54 of mass analyser 52 and by the mass-to-charge ratio of each ion whereby the ions in beam 38 having various mass-to-charge ratios can be passed consecutively to ion detector 46. Accordingly, ion detector 46 produces only a very small output (1 count or less per second) when mass analyser 52 is set to transmit ions having a specific mass-to-charge ratio and no ions having that mass-to-charge ratio are present in ion beam 38. Fig. 6B illustrates that the ion guide electrodes 58 and 58A shield the mass analyser entrance 55, that is, the projected areas of the entrance and exit ends of electrodes 58 and 58A cover the entrance area between the rods 54 of the mass analyser 52.

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Thus a mass spectrometer 10 as shown in Fig. 1, includes a source 12-16-24 for providing a beam of particles including ions 38 representative of chemical elements in the sample, a quadrupole mass analyser 52 and an ion detector 46 for receiving ions 38 from the beam of particles for spectrometric analysis whereby concentrations of different elements in the sample are determinable, an ion optics system 32-34-36-40-42 for establishing a reflecting electrostatic field between the source and the quadrupole mass analyser 52 for reflecting ions 38 from the particle beam thereby separating said reflected ions from neutral particles in the beam of particles, and a quadrupole ion guide 56 located adjacent the entrance 55 to the quadrupole mass analyser 52, wherein the reflecting electrostatic field directs the reflected ions 38 along a path (and focusses them) into the ion guide 56, the quadrupole ion guide 56 having electrodes 58 and 58A which are configured to divert the reflected ions 38 from the said path prior to their passage through the quadrupole mass analyser 52

and which shield the mass analyser entrance 55 as viewed in the direction of said path.

In the embodiments as illustrated in Figs. 2 to 5, features and components corresponding to those in the Fig. 1 embodiment have been accorded the same reference numerals and will not be further described. The differences between these embodiments resides in the configuration of the elongate electrodes of the respective ion guides 56. Thus Figs. 2 and 3 illustrate curved configurations for the ion guide 56 electrodes other than the preferred curved configuration of Fig. 1, such that the ions exit the quadrupole ion guide 56 generally in the same direction as said path along which they enter the quadrupole ion guide. Fig. 4 illustrates a non-curved configuration for the ion guide 56 electrodes for diverting the ions. Fig. 5 illustrates another curved configuration for the ion guide 56 electrodes for diverting the ions through an angle of 90° from said path. This embodiment allows a compact design for a mass spectrometer. With this embodiment, it would be advantageous to place a barrier under (as viewed in the Fig) the convex side of the ion guide 56 to prevent neutrals that might reflect off the electrodes 58, 58A reaching the detector 46 by bypassing the mass analyser 52.

20

To illustrate the improvements achieved with the present invention, Table 1 below shows some performance indicators for an inductively coupled plasma mass spectrometer having ion optics according to WO 00/17909 (PCT/AU99/00766) and the corresponding values for an inductively coupled plasma mass spectrometer according to the Fig. 1 embodiment.

25

Table 1

Ion optics	PCT/AU99/00766	Figure 1 of this disclosure
Sensitivity for Be ($m/z = 9$), counts per second per microgram per litre	500 - 10,000	70,000 - 110,000
Sensitivity for Mg ($m/z = 24$), counts per second per microgram per litre	20,000 - 100,000	250,000 - 400,000
Sensitivity for Co ($m/z = 59$), counts per second per microgram per litre	100,000 - 300,000	400,000 - 800,000
Sensitivity for In ($m/z = 115$), counts per second per microgram per litre	200,000 - 500,000	1,000,000 - 1,300,000
Sensitivity for Th ($m/z = 232$), counts per second per microgram per litre	600,000 - 1,000,000	650,000 - 1,000,000
CeO ⁺ /Ce ⁺ , %	3	<2.4
Ba ⁺⁺ /Ba ⁺ , %	<3	<2.7
Background at $m/z = 228$, counts per second	8-25	<1

- Although the above described embodiments are of mass spectrometers that employ a reflecting ion optics system, the invention may also be embodied in a mass spectrometer that employs an ion transmissive optics system. Such optics systems are known and thus not further described herein. It is also known for such systems to divert the sample ions from a particle beam to achieve separation of the sample ions from neutral particles and photons in the beam, thus providing an initial filtering stage. The provision of an ion guide

according to the invention in front of the mass analyser provides a second filtering stage in such mass spectrometers. The same as in the embodiments of Figs. 1-5, the electrodes of the ion guide of a mass spectrometer having an ion transmissive optics system must shield the mass analyser entrance in the
5 sense that any energetic neutral particles that are produced having either of the two possible components of motion as described hereinbefore are prevented from entering the mass analyser.

The invention described herein is susceptible to variations, modifications and/or
10 additions other than those specifically described and it is to be understood that the invention includes all such variations, modifications and/or additions which fall within the spirit and scope of the above description.

DATED: 27 April, 2001

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Figure 1

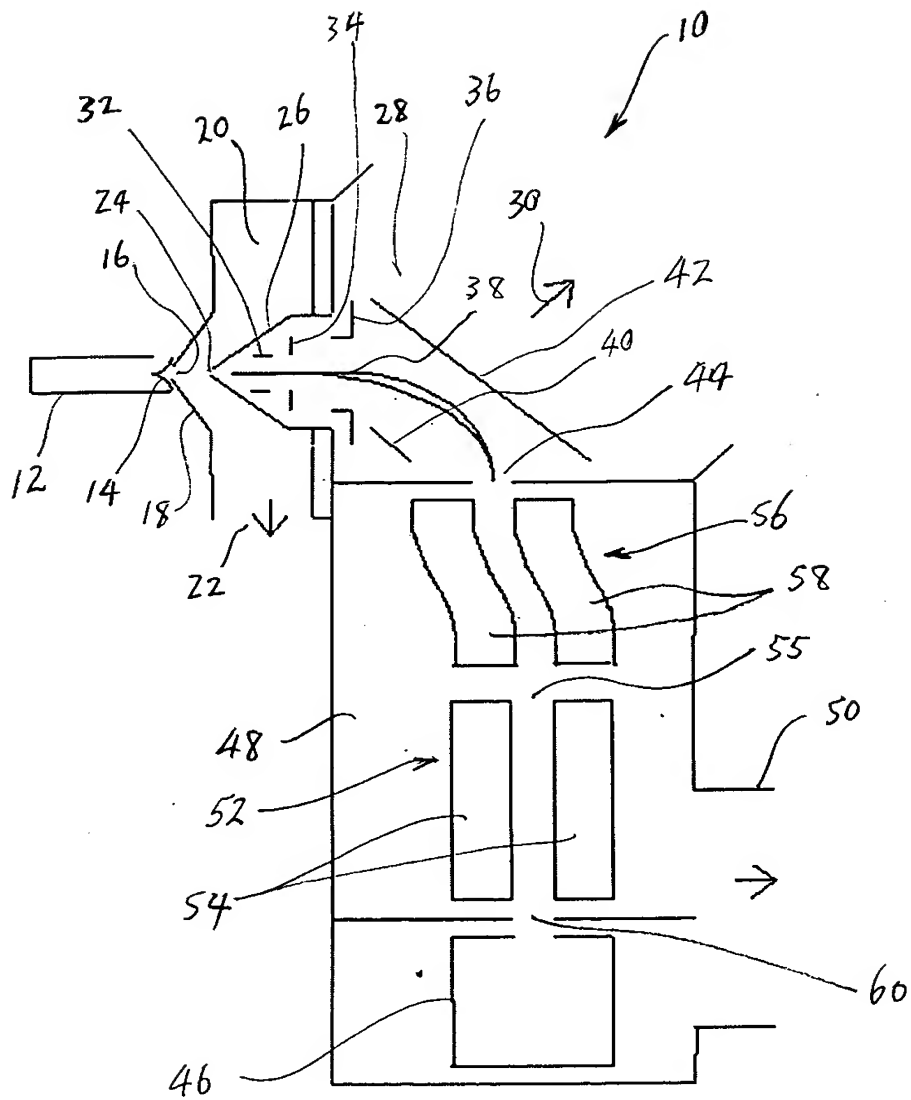
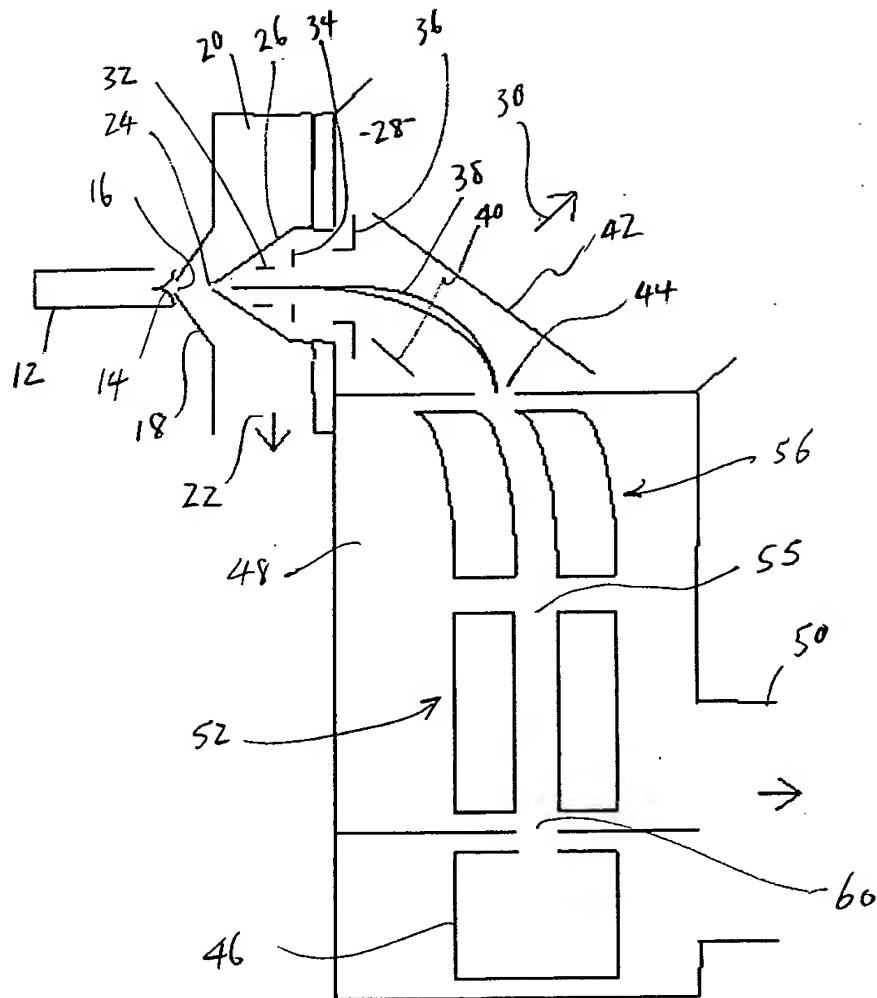
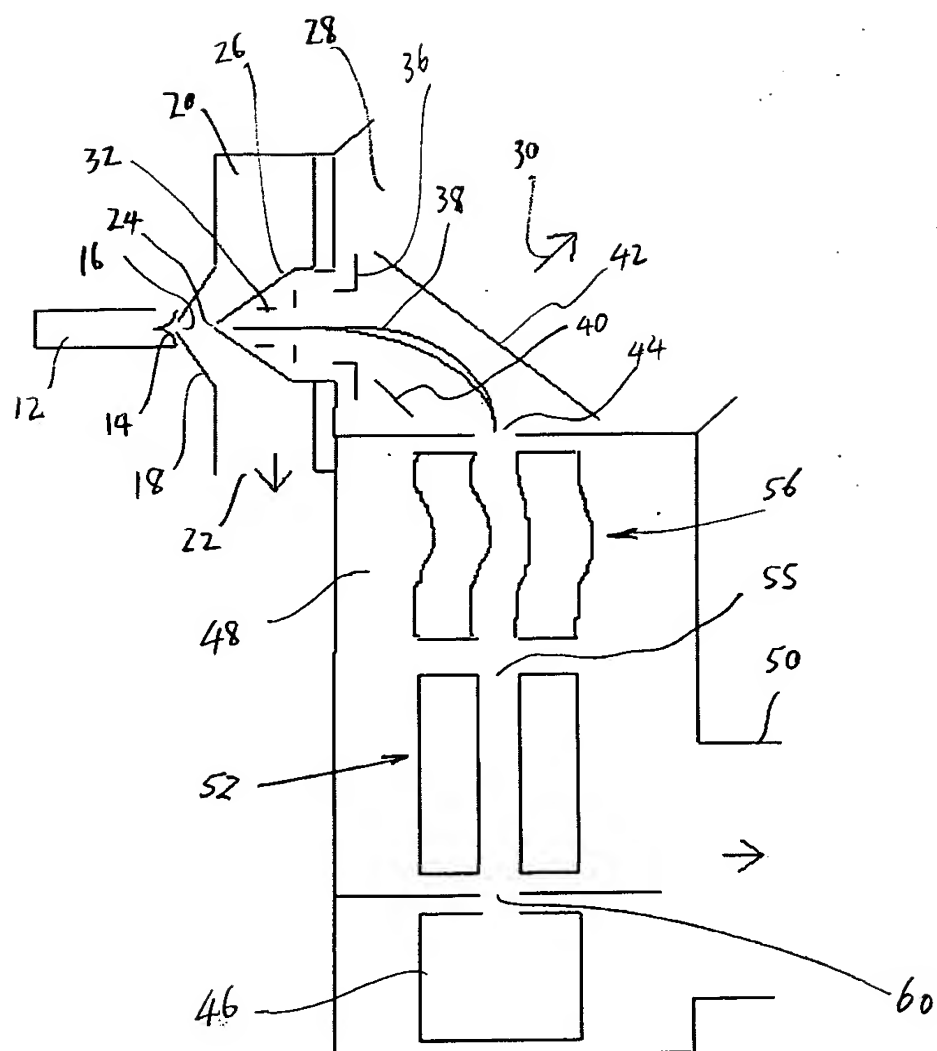


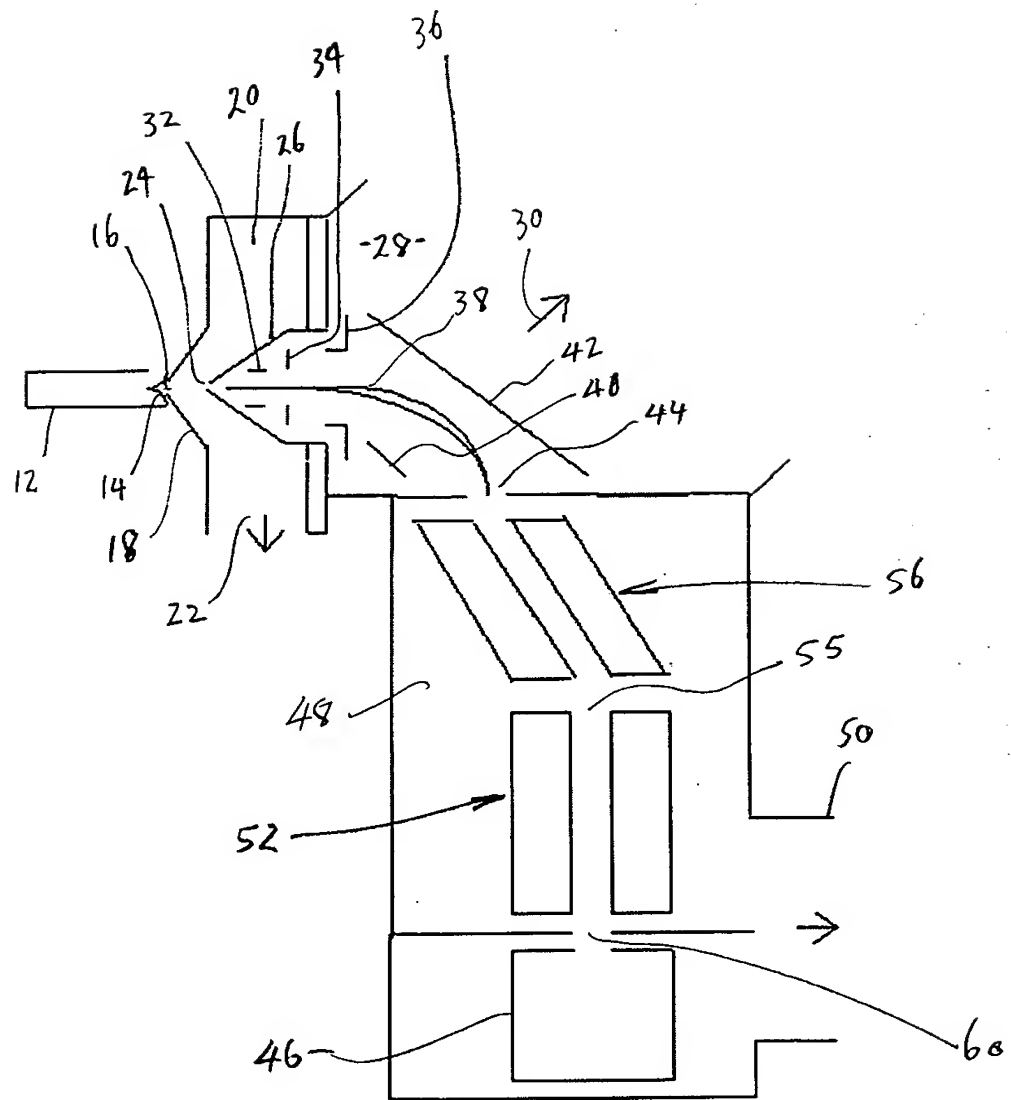
Figure 2





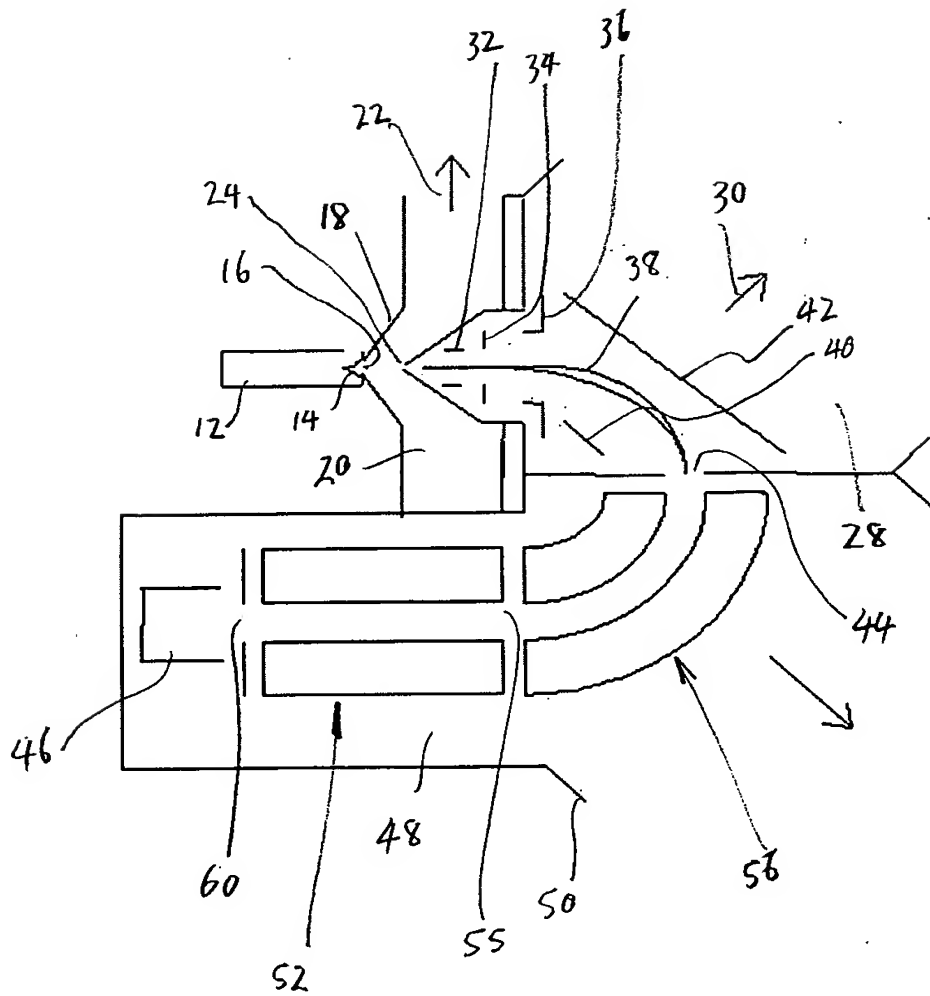
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Figure 4



5/6

Figure 5



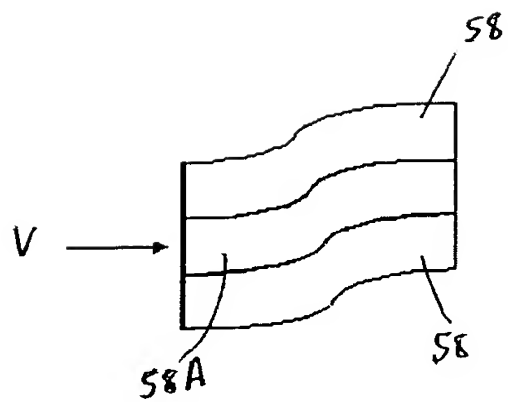


Figure 6A

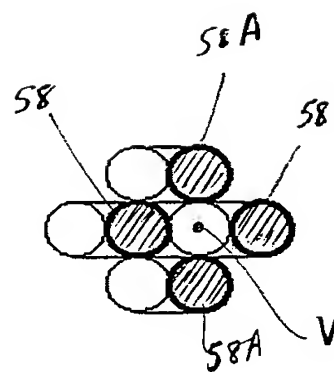


Figure 6B